High temperature memory in (Pb/La)(Zr/Ti)O_3 as intrinsic of the relaxor state rather than due to defect relaxation

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It has been recently shown that the memory of multiple aging stages, a phenomenon considered possible only below the glass transition of some glassy systems, appears also above that temperature range in the relaxor ferroelectric (Pb/La)(Zr/Ti)O_3 (PLZT). Doubts exist whether memory at such high temperature is intrinsic of the glassy relaxor state or is rather due to migration of mobile defects. It is shown that the memory in the electric susceptibility and elastic compliance of PLZT 9/65/35 is not enhanced but depressed by mobile defects like O vacancies, H defects and mobile charges resulting from their ionization. In addition, memory is drastically reduced at La contents slightly below the relaxor region of the phase diagram, unless aging is protracted for long times (months at room temperature). This is considered as evidence that in the non relaxor case memory is indeed due to slow migration of defects, while in the La rich case it is intrinsic of the relaxor state, even above the temperature of the susceptibility maximum.

I. INTRODUCTION

Relaxor ferroelectrics are under many aspects the electric analogue of spin glasses;[1,2] they are closely related to ferroelectrics, but with enough chemical disorder and/or frustrated interaction to transform the ferroelectric transition into a gradual freezing of the polar degrees of freedom, easily recognizable from the broad dielectric susceptibility maximum at a frequency dependent temperature $T_m(\omega)$. The characteristic relaxation time τ deduced from the relationship $\omega\tau \sim 1$ at the maximum diverges at a finite temperature T_f approximately following the Vogel-Fulcher law $\tau = \tau_0 \exp[E/(T - T_f)]$, or a power law, $\tau = \tau_0 \left(\frac{T-T_f}{T_f}\right)^{z\nu}$, and T_f can be considered as an indication of the freezing temperature or glass transition. In addition, these materials exhibit aging, rejuvenation and memory; such phenomena, usually observed and studied below T_f, appear in the electric susceptibility $\chi(\omega, T)$ but also elastic compliance $s(\omega, T)$ as a slow isothermal decrease (aging); on further cooling, the susceptibilities increase again joining the reference curve $\chi_{\rm ref}(\omega, T)$ measured during continuous cooling (rejuvenation); during reheating, the hole in the $\chi(\omega, T)$ curve created by aging may be partially retraced (memory). Aging in relaxor ferroelectrics has been found as early as 1980,[3] but only recently the non-equilibrium phenomena have started to be studied in this class of materials. Aging is a rather frequent phenomenon with various possible causes, but rejuvenation and especially memory are considered as peculiar of the frozen spin glass state,[4] and theoretical models for them rely on a proliferation of hierarchically organized metastable states below a glass transition temperature,[5] or the vanishing of the barriers between these metastable states above a temperature T_f.[6] Memory is therefore expected to vanish above T_f, but it has been observed also above that temperature in few systems: in the magnetic perovskite $Y_{0.7}Ca_{0.3}MnO_3$, which presents an unusual state of short-range ferromagnetic order before freezing into a canonical spin glass state;[7] in the relaxor ferroelectric (Pb/La)(Zr/Ti)O_3 (PLZT)[8] and to some extent in $Pb(Mg_{1/3}Nb_{2/3})_{1-x}Ti_xO_3$ (PMN-PT)[9] but not in PMN.[8] A detailed study[8] showed that the memory recovery of aging stages at a temperature T_a becomes anomalously high when T_a approaches T_f from below and remains high above T_f in PLZT, instead of vanishing as in PMN or in spin glasses; for this reason, it was proposed that high-temperature aging below and above T_f in PLZT are of different nature, the latter possibly being related to mobile defects like oxygen vacancies. Indeed, such defects are held responsible for the closely related phenomena of fatigue and domain wall clamping in ferroelectrics,[10] which also involve a slow decrease of the dielectric susceptibility. On the other hand, we showed[11] that PLZT has even memory of *multiple* aging stages above T_f. Memory of multiple aging stages has never been observed – and probably not looked for – outside a canonical spin glass[12,13] and possibly superparamagnetic[14,15,16] state; therefore, its presence is already an indication that in PLZT some mechanism of hierarchically organized correlations intrinsic of the relaxor state is involved also above the relaxor transition, rather than marginally mobile defects.[11] Still, in the absence of a quantitative model for the contribution of mobile defects on aging and memory, the possibility cannot be excluded that defects are the cause of such non equilibrium phenomena above T_f, also because O defects up to few tenths of molar percent may arise from the compensation of unavoidable deviations from the ideal cation stoichiometry.

It is our purpose here to study the influence of O vacancies and H impurities on aging and memory in the region near and above T_f in PLZT, since these are the only defects whose mobility might produce relaxation ef-

fects with characteristic times of the order of hours or days at such temperatures (300-400 K). In fact, O is by far more mobile than the cations, with an activation energy for diffusion of ~ 1 eV in titanate perovskites,[17,18] and the only possible O defect is a vacancy, since there would not be room enough for interstitial O in the closely packed perovskite structure. Hydrogen may enter as $(OH)^-$ ion substituting an O vacancy and its diffusion barrier is even lower.[19] Regarding the off-centre ionic displacements, they are fully responsible for the dielectric and relaxor properties of these materials and cannot be considered as extrinsic defects affecting memory. Finally, mobile charges from non compensated or ionized defects might be considered responsible for anomalous non-equilibrium phenomena, but they also produce thermally activated relaxation processes in the dielectric spectra at high temperature, that are not observed in PLZT.

II. EXPERIMENTAL

We tested two compositions of $(Pb_{1-x}La_x)(Zr_yTi_{1-y})_{1-x/4}O_3$: one, with $x = 0.09$, $y = 0.65$ (PLZT 9/65/35) and charge compensating vacancies in the Zr/Ti sublattice, is well within the relaxor state below $T_f < 340$ K; such a composition has been extensively investigated in the literature,[8,11,20,21] and the sample was the same used in previous work where we observed multiple memory at relatively high temperatures.[11] The other composition was $(Pb_{0.93}La_{0.07})(Zr_{0.6}Ti_{0.4})_{0.96}Nb_{0.01}O_{3-\delta}$ (PLZTN 7/60/40), with $x = 0.07$, $y = 0.60$, and 1% substitutional Nb and a slight excess of charge compensating vacancies in the Zr/Ti sublattice; the cation charge is 5.96 per formula unit, requiring 0.02 O vacancies for the charge neutrality condition. According to the PLZT phase diagram,[20] PLZTN 7/60/40 is at the border between ferroelectric and relaxor state below $T_C \simeq 460$ K.

The ceramic samples have been prepared by the mixed-oxide method; the starting oxide powders were calcined at 850 °C for 4 hours, pressed into bars and sintered at 1250 °C for 2 h, packed with $PbZrO_3$ + 5wt% excess ZrO_2 in order to maintain a constant PbO activity at the sintering temperature. The absence of impurity phases was checked by powder X-ray diffraction. The ingots were cut into thin bars approximately $45 \times 4 \times 0.5$ mm^3. The electrodes for the anelastic and dielectric spectroscopy measurements were applied with silver paint and the samples were annealed in air at 700 °C for avoiding any effects from the possibly damaged surfaces after cutting. The introduction of O vacancies into PLZT 9/65/35 was first attempted by heating up to 660 °C in vacuum down to 2×10^{-8} mbar, obtaining an irregularly darker sample surface; a more drastic reducing treatment was therefore made in 800 mbar of H_2 at 690 °C for 90 min. The latter treatment changed the sample color into very dark and uniform gray; assuming that the only effect of the treatment was O loss (without H uptake and no effect on the Ag electrodes), the mass reduction corresponded to an introduction of 3.3×10^{-3} O vacancies per formula unit and, judging from the results of similar treatments on $SrTiO_3$,[18] it is likely that some H entered the sample.

The dielectric susceptibility $\chi = \chi' - i\chi''$ was measured with a HP 4194 A impedance bridge with a four wire probe and a signal level of 0.5 V/mm, between 200 Hz and 1 MHz. The measurements were made on heating/cooling at ± 1.5 K/min between 520 to 240 K in a Delta climatic chamber. The chamber was enclosed in a sealed box that was flushed with dry nitrogen in order to prevent the condensation of water on the sample from air during cooling; otherwise, during subsequent heating the condensed water would shortcut the electrodes giving rise to anomalies in the spectra.

The dynamic Young's modulus $E(\omega, T) = E' + iE''$ or its reciprocal, the elastic compliance $s = s' - is'' = E^{-1}$, was measured by electrostatically exciting the flexural modes of the bars suspended in vacuum on thin thermocouple wires in correspondence with the nodal lines; the 1st, 3rd and 5th modes could be measured, whose frequencies are in the ratios $1 : 5.4 : 13.3$, the fundamental frequencies of the PLZT 9/65/35 and PLZTN 7/60/40 samples being $\omega/2\pi \simeq 1$ and 0.7 kHz respectively. The real part of the Young's modulus is related to the resonance frequency through $\omega_n = \alpha_n \sqrt{E'/\rho}$, where α_n is a geometrical factor of the n-th vibration mode and ρ the mass density. The latter varies with temperature much less than E', so that $\omega^2(T)/\omega^2(T_0) \simeq E(T)/E(T_0) = s(T_0)/s(T)$. The elastic energy loss coefficient, or the reciprocal of the mechanical quality factor,[22] is $Q^{-1}(\omega, T) = E''/E' = s''/s'$; the Q^{-1} was measured from the decay of the free oscillations or from the width of the resonance peak. The elastic compliance s is the mechanical analogue of the dielectric susceptibility χ, with Q^{-1} corresponding to $\tan\delta$. The absolute value of s is difficult to be evaluated, due to sample porosity, slightly irregular shape and to the contribution from the Ag electrodes; therefore the s' curves will be normalized with respect to the value s_0 extrapolated to very high temperature. The heating and cooling rates during the anelastic experiments were of $0.8 - 1$ K/min. All the anelastic and dielectric measurements started from above 500 K, in order to erase any previous history.

III. RESULTS

A. The relaxor PLZT 9/65/35

1. *Dielectric measurements*

The dielectric constant χ' and losses $\tan\delta = \chi''/\chi'$ of PLZT 9/65/35 are shown in Fig. 1, measured both on cooling down to 240 K at -1.5 K/min (continuous lines) and on subsequent heating at 1.5 K/min (filled

symbols). Only two frequencies, 1 and 100 kHz, are shown, but the measurements were extended between 200 Hz and 1 MHz, and gave the usual result found in the literature.[11,21,23] Notice the merging into a single curve of the χ' curves at high temperature and of the χ'' ones at low temperature (see also Refs. 11,24 on the same and similar samples), characteristic of the spin glass susceptibilities. As usual for glassy systems, it is possible to define a characteristic relaxation time τ from the condition $\omega\tau(T_m) = 1$ at the maximum of χ', and to fit it with a Vogel-Fulcher law, $\tau = \omega = \tau_0 \exp[E/(T_m - T_f)]$ or a power law, $\tau \sim \left(\frac{T-T_f}{T_f}\right)^{-z\nu}$, where the temperature T_f at which the characteristic time diverges indicates the freezing temperature or the glass transition. This analysis with the present samples yields[11] $T_f = 320$ K for the Vogel-Fulcher and 337 K and $z\nu = 6.8$ for the scaling approach, without the possibility of clearly distinguishing which one is the better description; it is however clear that the freezing temperature for the polar fluctuations is lower than 340 K. Also shown in Fig. 1 with empty symbols is χ measured at 1 kHz on cooling, after the reduction treatment in H_2 atmosphere. The peak in the real part is slightly shifted to lower temperature and enhanced in intensity, while the losses acquire an intense thermally activated contribution at high temperature, attributable to the relaxation of mobile charges introduced by the O and H defects.

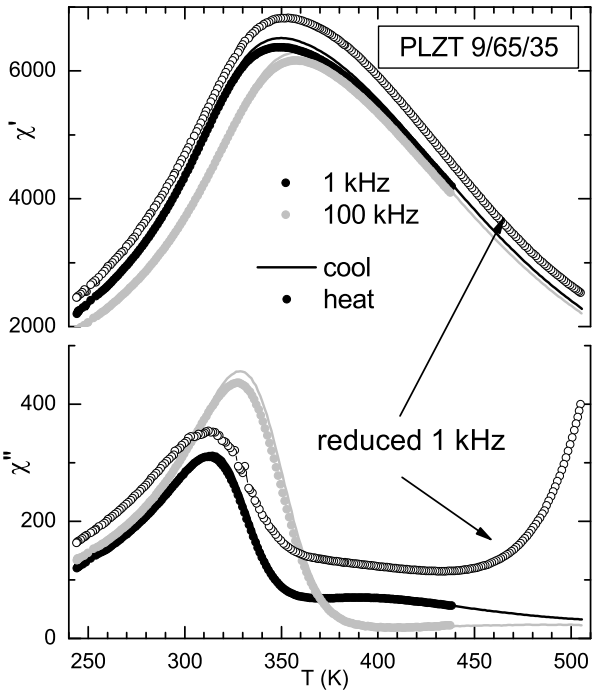

FIG. 1: Real and imaginary dielectric susceptibility of PLZT 9/65/35 measured during cooling and heating at ±1.5 K/min (reference curves). Black and gray refer to 1 and 100 kHz respectively. The empty symbols are the cooling curves after reducing the sample in H_2 atmosphere.

A weak relaxation in χ'', with maximum around 400 K at 1 kHz, appears also in the oxygenated state; this was originally absent, as shown in Ref. 11, and is probably due to the fact that the sample has been repeatedly subjected to reducing and oxygenation treatments, from which it did not recover completely. This fact does not weaken the present conclusions, since the memory of even multiple aging stages is found also in the pristine state[11], and the "oxygenated" and "reduced" state considered here certainly differ considerably in the amount of defects, as demonstrated by the curves in Fig. 1 and the changes in sample color.

2. Dielectric aging, rejuvenation and memory

Figure 2 presents the effect of aging 24 h at 373 K, well above the freezing temperature or glass transition, $T_f <$ 340 K. The quality of the data is better in χ' rather than in $\tan\delta$, especially after the reduction treatment, and therefore we will consider the $\chi'(\omega, T)$ curves measured at $\omega/2\pi = 1$ kHz, but very similar results are obtained at the other frequencies.

After dividing by the cooling and heating reference curves (Fig. 1 and continuous lines in Fig. 2a), one obtains the left half of a negative peak from the cooling curve after aging and a slightly smaller peak from the heating curve, where the fraction of memory recovery can be defined as the ratio between the intensities of the two peaks. The case of the well oxygenated PLZT 9/65/35 is rather clear-cut, with the $\chi'(\omega, T)$ curves overlapping almost perfectly (better than 0.3%) onto the reference curves below the aging temperature (perfect rejuvenation) and above it. We operatively define the memory recovery in a manner that works also for the less regular curves obtained after reduction, as the ratio

$$r = \frac{\chi'(T_a)/\chi'_{\text{ref c}}(T_a)}{\chi'(T_{\min})/\chi'_{\text{ref h}}(T_{\min})}\,, \qquad (1)$$

where $\chi'_{\text{ref c}}$ and $\chi'_{\text{ref h}}$ are the reference curves on cooling and heating, $\chi'(T_a)$ is the dielectric susceptibility at the end of aging at $T_a = 373$ K and $T_{\min}$ is the temperature of the minimum of $\chi'(T)$ on heating, slightly smaller than T_a. This is the most straightforward definition of memory recovery, taking into account the fact that the curves measured on heating are slightly lower than those measured on cooling. Applying this criterion to all the measured frequencies between 200 Hz and 1 MHz, one gets a memory recovery of 84.6%±0.5% for the dielectric susceptibility.

The experiment was repeated on a sample reduced in H_2, as described in Sect. II, and therefore with a considerably higher amount of O vacancies and mobile charges, now appearing in the dielectric losses at high temperature (Fig. 1).

In the reduced sample, the rejuvenation curve is ∼ 1% higher than the reference near the aging hole, and remains high during heating. Applying the above criterion

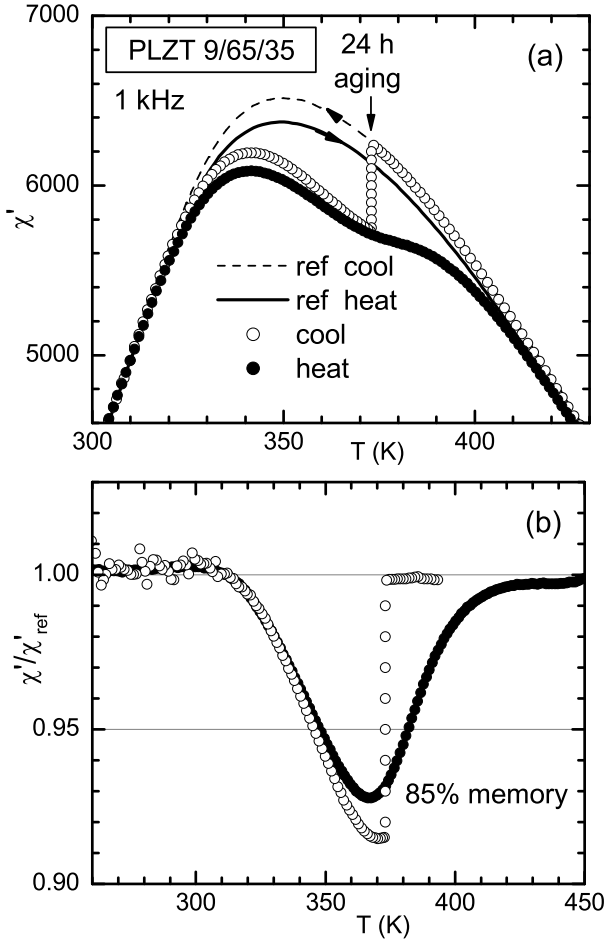

FIG. 2: Aging, rejuvenation and memory of PLZT 9/65/35. (a) raw data, including the reference curves measured during continuous cooling and heating; (b) data normalized with respect to the corresponding reference curves.

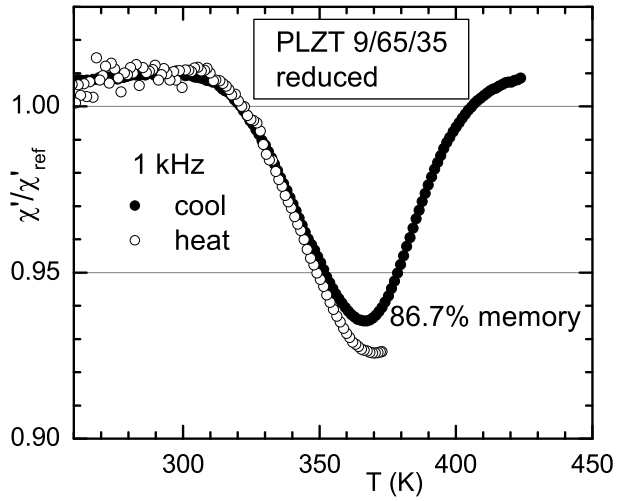

FIG. 3: Aging, rejuvenation and memory of a PLZT 9/65/35 sample after reduction in H_2 atmosphere, to be compared with Fig. 2b. The $\chi'_{\rm ref}$ reference curve on cooling is shown in Fig. 1.

to all the measured frequencies one gets a memory recovery of $86.6\% \pm 0.5\%$, only 2% higher than in the defect free material. Considering the sensitivity of the $\chi(T)$ curves to changes in the temperature rate, especially in the reduced state, we can say that the introduction of O and H related defects affects the aging behavior but there is no enhancement of the memory recovery within experimental error.

3. Anelastic measurements

The same type of experiments has been made with the dynamic compliance, which has already been shown to exhibit closely similar non-equilibrium effects.[11] There are however some differences due to the fact that *i)* there is a strong contribution of the lattice to s', besides that related to the polar fluctuations, and therefore the fraction of s' that exhibits aging and memory is smaller than in the dielectric experiment, by more than three times in the present case; *ii)* the dynamic compliance is sensitive to the strain fluctuations, of quadrupolar nature, rather than directly to the electric dipolar ones, and the maximum of the elastic losses is shifted to lower temperature;[24] therefore, it becomes very difficult to reliably measure aging and memory phenomena in the $Q^{-1}(\omega, T)$ curves at $T \geq 350$ K, where the losses become comparable with the background. For these reasons, we chose to study the effect of O vacancies in PLZT 9/65/35 at 326 K both in the $Q^{-1}(T)$ and $s'(T)$ curves measured at 1 kHz. This temperature is 50 K lower than that of the dielectric experiment, but still within the temperature range where Colla *et al.* found that the memory recovery becomes anomalously high, instead of vanishing as in PMN.[8]

Figure 4 shows the raw data of the cooling and heating reference curves of the normalized dynamic compliance s'/s_0 and elastic energy loss coefficient $Q^{-1} = s''/s'$ at $\simeq 1$ kHz, together with the effect of aging for 26 h at 325 K, rejuvenation and memory. The result of normalization with the reference curves is shown in Fig. 5(a) for s'; the Q^{-1} curves give exactly the same result but are more noisy. The fact that the data on cooling before aging differ from 1 is due to the difficulty of stopping the temperature of the sample suspended in vacuum, but this is inessential after 26 h of aging. The memory recovery is total, or even 104% by applying the criterion used for the dielectric memory. The result of the same experiment after reduction in H_2 atmosphere is shown in Fig. 5(b); in this case the memory recovery is definitely lowered of at least 10%.

B. The nearly ferroelectric PLZTN 7/60/40

Figure 6 presents the reference dielectric curves of the PLZTN 7/60/40 sample, again at 1 and 100 kHz. As expected from the phase diagram of PLZT, this compo-

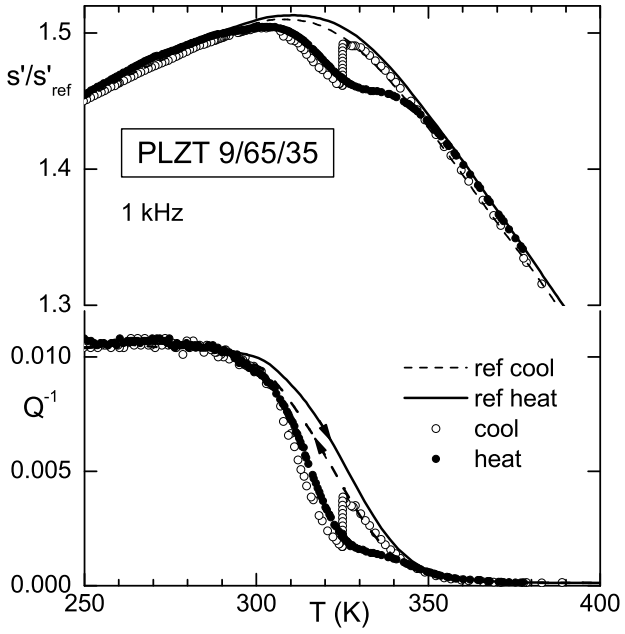

FIG. 4: Normalized dynamic compliance s'/s_0 and elastic energy loss coefficient $Q^{-1} = s''/s'$ of PLZT measured at $\simeq$ 1 kHz. Broken and continuous lines: cooling and heating reference curves; open and closed symbols: cooling with 26 h aging and rejuvenation and heating with memory.

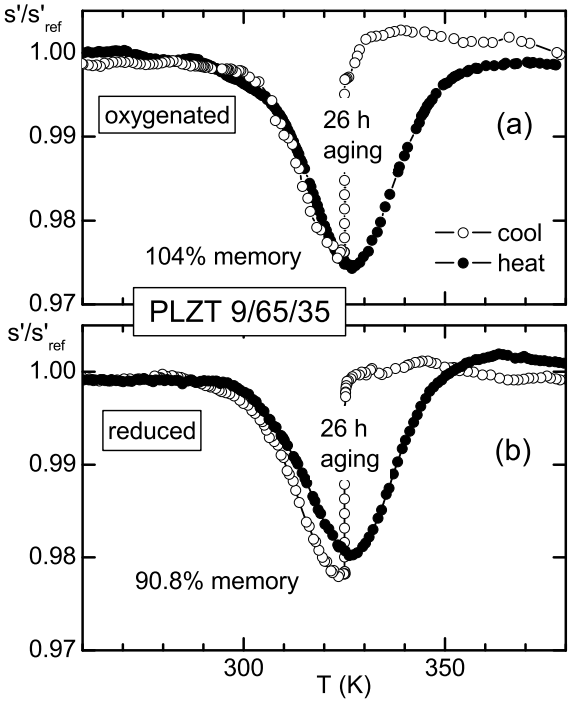

FIG. 5: Aging, rejuvenation and memory of PLZTN 7/60/40 after normalization with the cooling and heating reference curves (see Fig. 5).

sition is at the border between the relaxor and the ferroelectric states:[20,23] the dispersion in frequency of the maximum in χ' is very weak, and the curves measured on heating (full circles) are lower than those measured during cooling (continuous lines) up to $T_{\rm FE}$ = 370 K, indicating the formation of a partial ferroelectric order, which disappears on heating above $T_{\rm FE}$.

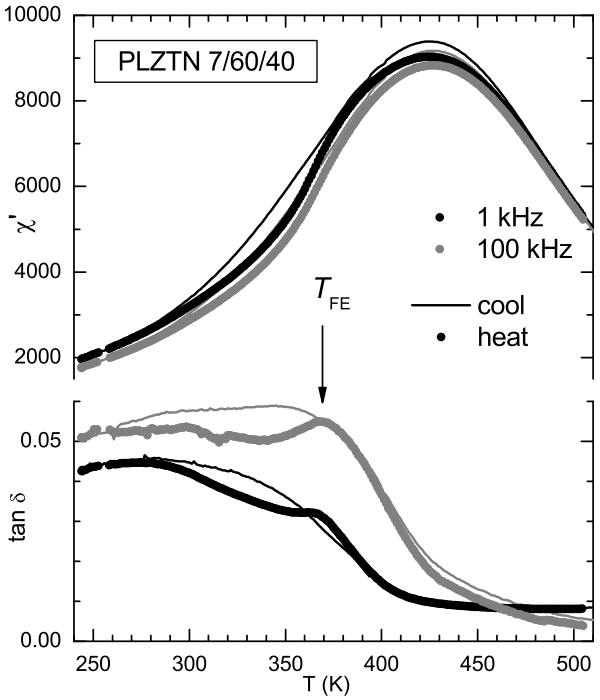

FIG. 6: Dielectric susceptibility and losses of PLZTN 7/60/40 measured during cooling and heating at ±1.5 K/min.

The result of aging 21 h at 350 K is shown in Fig. 7 for the compliance; the initial aging rate is fast compared to the relaxor phase, as appears from the departure from the reference cooling measurement already below 360 K, when the cooling rate was slowed down to stop at $T_a = 350$ K. After aging, the cooling was stopped already 35 K below T_a, but this was sufficient to erase almost completely the memory of the aging stage; the recovery of the hole in the Q^{-1} curve was no more than 30%, and that in s' was almost unmeasurable, also due to significant departure from the reference curve. We did not make a systematic study of the influence of the amplitude of the temperature excursion below T_a on the memory recovery, but it is clear that memory in this partly relaxor and partly ferroelectric composition is far less clean and complete than in the pure relaxor phase, where there is practically no effect of the low temperature excursion, and there is good reproducibility between heating and cooling curves outside the aging hole.

This fact can be seen also in Fig. 8, where the effect of 13 days aging at room temperature is almost completely erased by cooling 70 K below T_a (circles, the memory is no more than 15%). Note that in this case

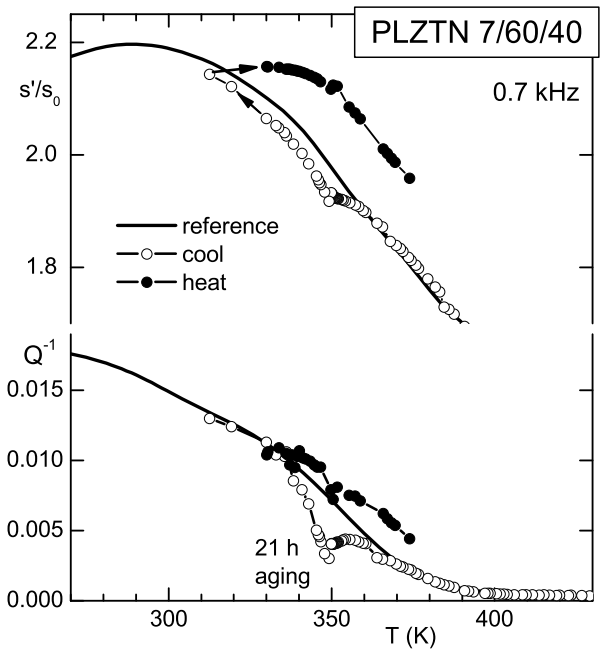

FIG. 7: Normalized elastic compliance s' and elastic energy loss coefficient $Q^{-1}$of PLZTN 7/60/40 measured at 0.7 kHz during continuous cooling at -0.8 K/min (line); cooling with aging at 350 K (empty circles) and subsequent heating (filled circles).

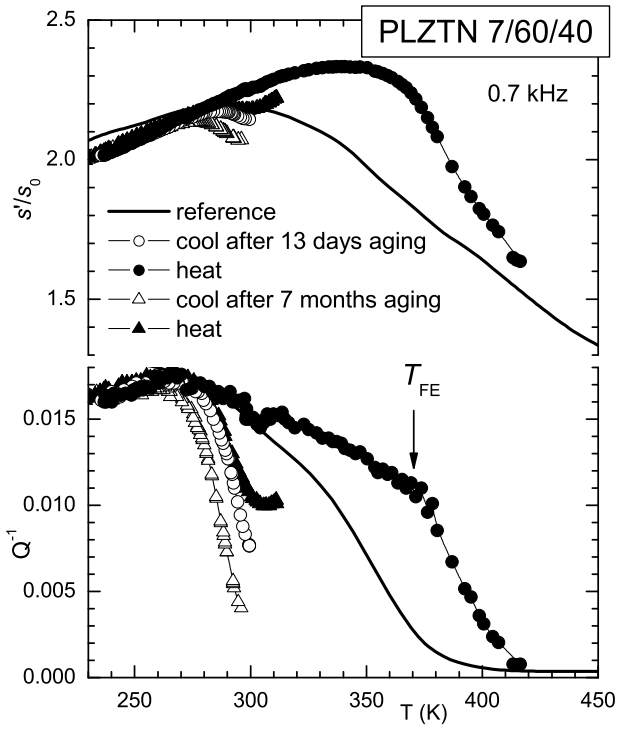

FIG. 8: Normalized compliance and elastic energy loss coefficient of PLZTN 7/60/40 after 13 days aging at room temperature + cooling down to 225 K (circles) and 7.5 months aging + cooling to 235 K (triangles). The continuous line is the reference curve on cooling.

it is $T_a \sim 0.7T_m$, $T_m \simeq 430$ K being the temperature of the maximum in dielectric susceptibility, and at $0.7T_m$ relaxor PLZT 9/65/35 and spin-glass systems have full memory recovery. A more substantial and stable memory is observed after 7.5 months aging at room temperature (triangles, $\sim 70\%$ recovery). Note also that the losses on heating remain higher than during cooling, but abruptly decrease above the same $T_{\rm FE}$ determined by the dielectric measurement.

IV. DISCUSSION

The aim of these experiments is to evaluate the possible contribution of extrinsic defects to the memory of aging stages found in the relaxor PLZT 9/65/35 also near and above the freezing temperature T_f. The following discussion does not rely on a precise definition of T_f for PLZT, and we will also assimilate it to the temperature T_m of the maximum of χ'' at some low frequency.[8] The reason why one might expect some mechanism extrinsic with respect to the relaxor transition, is that it is generally accepted that aging to some extent and particularly rejuvenation and memory need some hierarchical organization of the microscopic states and interactions, which is expected to arise only below a glass transition.[4,16,25,26,27]

An extensive investigation on the memory in relaxors has been conducted by Colla and coworkers[8] on PLZT 9/65/35, PMN and PMN-PT. These authors found that PMN behaves like a canonical spin glass, with its memory of an aging stage at T_a vanishing when T_a approaches T_m from below. Instead, the memory of PLZT 9/65/35 has an initial decrease with a minimum around $T_a = 0.85T_m$ and then rises again to 80% at T_m, remaining high up to $1.15T_m$. The comparison of the memory recovery versus T_a in PMN and PLZT together with the above considerations indeed suggests that a different mechanism exists above T_f in PLZT, which the authors identify with mobile defects.

To our knowledge, the only defects whose mobility may be high enough to match with the temperature and characteristic times of these aging experiments are: mobile charges (electrons or holes) from ionized defects, O vacancies and hydrogen, generally associated in the form of $(OH)^-$ ion in perovskites.[19] In the present study, we tested all these possibilities.

The reference relaxor composition has a rather clear-cut behavior, typical of spin-glasses:[6,11,28] almost overlapping cooling and heating reference $\chi(\omega,T)$ curves, with no frequency dependence in the low-temperature $\chi''(\omega,T)$ and high-temperature $\chi'(\omega,T)$ (Fig. 1), complete rejuvenation on cooling, heating curves with sub-

stantial or complete memory recovery and good matching with the reference far from T_a; in addition, one day aging is sufficient to imprint a complete (Fig. 5a) or almost complete (Fig. 2) memory of the aging stage. The only peculiarity is that memory exists both below and above T_f. Now, if the high temperature memory were almost completely due to defects, it should be considerably enhanced after reduction in H_2. In fact, such a treatment introduced at least 3.3×10^{-3} O vacancies per formula unit, as deduced from the mass loss, and most likely also H defects, whose amount we cannot evaluate; as a result, the sample turned from white-yellow to dark grey and an extremely intense thermally activated relaxation process appeared in the high temperature side of χ'', presumably due the motion of charges from the new ionized defects. The reduced sample therefore contains a substantially larger amount of all the mobile defects considered before, with respect to the standard oxygenated state. The effect on the memory recovery of high temperature aging, however, is negligible in the dielectric case (2% increase, Fig. 3) and consists in a depression of over 10% in the anelastic one (Fig. 5); note that during the anelastic experiment aging has been done at a temperature 50 K lower than in the dielectric one, and this should be the main reason for the larger initial memory recovery and larger loss after reduction.

Regarding the differences between the dielectric and anelastic measurements, it can be observed that the dynamic compliance s probes quadrupolar strain fluctuations, while the dielectric susceptibility probes dipolar polarization fluctuations, and therefore the χ and s curves may differ.[24] In principle, there may be relaxation modes appearing in s and not in χ and *vice versa*, but in practice there is correlation between strain and polarization fluctuations. For example, in a perfect crystal the inversion of an electric dipole causes no change in strain (which is centrosymmetric), while rotations of the O octahedra cause strain but no polarization changes; in a disordered crystal like PLZT, however, there are no pure inversions of dipoles or pure rotations of octahedra, and different modes are coupled together.[24] We do not know whether, between anelastic and dielectric responses, one is more significant than the other for studying nonequilibrium processes. Certainly, the dielectric response is more directly related to the dipolar interactions, which presumably govern the dynamics of relaxor ferroelectrics; on the other hand, the anelastic response truly probes the bulk and is insensitive to mobile charges, unlike χ in reduced or defective samples.[29]

In the second part of the experiment, we tested the composition PLZTN 7/60/40, which, although very close to PLZT 9/65/35, presents differences with respect to the non-equilibrium phenomena: *i)* PLZT 9/65/35 supports a full relaxor state and in the standard oxygenated state has no detectable extrinsic mobile defects, like O vacancies; *ii)* PLZTN 7/60/40 presents both relaxor-like susceptibility maximum and, below $T_{FE} = 370$ K, weak ferroelectric properties and should have about 2% of O vacancies in order to balance the cation charge (see Experimental). Therefore, besides having a large amount of defects, PLZTN 7/60/40 starts developing ferroelectric domains below T_{FE}; if anomalous memory phenomena may arise from mobile defects interacting with polar nanodomains and/or more developed ferroelectric domains, then such phenomena should be particularly well developed in PLZTN 7/60/40. Again, the experiment shows that this is not case; rather, the non equilibrium processes related to the relaxor state and to mobile defects have quite different phenomenologies and time scales. Figure 7 shows that the memory of an aging stage of 21 h at $T_a = 350$ K is drastically lower than in the full relaxor case: the value of T_a is included between those of the dielectric and anelastic aging experiments in PLZT 9/65/35, so that defects have the same mobility in all the experiments; still, even though cooling is extended only to 35 K below T_a, compared to the 100 K of the previous cases, the memory recovery is less than 30%. In addition, when the formation of ferroelectric domains, although small and disordered, starts, the behavior on cooling and heating is far less reproducible than in the relaxor case. Figure 8 shows the effect of extending cooling down to 230 K, as in the experiments with PLZT 9/65/35, after longer aging stages at room temperature: a 13 days aging causes a marked decrease of both s' and s'', but negligible memory on heating. This demonstrates that the combination of small or even more developed ferroelectric domains and mobile defects, although causes aging, is not able to create the memory effects found in the relaxor state. Rather, the slow reorientation and migration of O vacancies within the strain and electric fields of ferroelectric domains may be responsible for the memory imprinting on the much longer time scale of months (triangles in Fig. 8). The closely related phenomena of domain wall clamping[10] and formation of internal fields[30] from mobile defects adapting themselves to domains are known to occur in ferroelectrics.[31]

A. Possible origin for memory above the freezing temperature

It remains to be explained how is it possible that in PLZT memory of even multiple aging stages, as also shown in previous work,[11] may occur above the temperature of the maximum in the susceptibility. The reason for this behavior may reside in the fact that, unlike spin glasses, the polar degrees of freedom in relaxor ferroelectrics freeze out of an already partially correlated state. In fact, relaxor ferroelectrics are characterized by the Burns temperature $T_B \gg T_f$, below which the formation of polar nanoclusters starts;[1,2] therefore, the state below T_B is a sort of supeparaelectric one, and the analogy between relaxors and magnetic systems is probably more appropriate with strongly correlated superparamagnets rather than with canonical spin-glasses, where the dynamics above T_f is that of individual spins,

although interacting. Indeed, the magnetic perovskite $Y_{0.7}Ca_{0.3}MnO_3$, presents a spin glass state preceded by short-range ferromagnetic order, reminiscent of the polar nanoclusters of relaxors, and also exhibits memory above the spin glass transition.[7] The authors found this behavior unusual and were not able to classify it according to any available theory, but suggested that it may be related to the phase-separated nature of manganites. In ferroelectric relaxors no electronic phase separation occurs, but certainly the analogy with $Y_{0.7}Ca_{0.3}MnO_3$ suggests that highly correlated and hierarchically organized states may arise also from the interactions among the polar or magnetic clusters, which on further cooling freeze into the relaxor or spin-glass state. It should be remarked that, in order to explain memory, the need of hierarchical or at least strongly correlated dynamics, opposed to simple broad distribution of relaxation times, is not only indicated by the available theoretical models, but also by experiments on superparamagnets.

Magnetic nanoparticle systems can be made with a controlled distribution of particle sizes and with different degrees of dipolar interaction among the particles. It is therefore possible to obtain slow dynamics in systems ranging between two limits: *i)* weakly interacting particles with a broad distribution of individual relaxation times, due to a broad distribution of their sizes, and *ii)* strongly interacting particles with collective dynamics. Both limits exhibit various forms of non-equilibrium dynamics below some blocking temperature T_b, which from the phenomenological point of view corresponds to T_f in spin-glasses. Even systems belonging to the first category may exhibit some kind of memory; memory of multiple aging stages has been found in the dc magnetization of weakly interacting superparamagnets,[14,15] where the $M(T)$ curve on heating retraces, although smoothly, the steps formed during previous field cooling with aging stages at zero field. It has been remarked, however, that such a behavior can be completely accounted for in terms of broad distribution of relaxation times, and that these systems lack memory in the ac susceptibility under zero field.[15] Instead, memory in zero field cooled experiments can be found only in strongly interacting superparamagnets, also called superspin glasses.[16] The analogy between relaxor PLZT and superspin glasses, however, is not straightforward, since the latter exhibit aging and memory below a blocking temperature that is the equivalent of T_f in spin glasses, and we are not aware of experiments in such systems where it has been verified that these phenomena occur also above the temperature of the maxima in the ac susceptibilities.

A successful attempt in modeling aging and memory in the dynamic susceptibility has been made by Sasaki and Nemoto,[25] through the Multi-layer Random Energy Model; the main hypothesis is that the states of the system are hierarchically organized into "layers", where the n-th layer contains states that can access the $n+1$-th layer by overcoming energy barriers E distributed according to $p(E) \propto \exp(-E/T_C(n))$, with $T_C(n+1) > T_C(n)$ and $1 \leq n \leq L$. In this manner it is possible to reproduce by numerical simulation memory effects in $\chi''(t)$ during aging stages below $T_C(L) \equiv T_f$. It would be interesting to also know the shapes of the $\chi(\omega, T)$ curves resulting from this model, in order to correlate the maximum temperature at which memory is found with the maxima in $\chi(\omega, T)$. The $\chi(\omega, T)$ in the limiting case of a single layer can be analytically approximated,[32] and has been used to describe the susceptibility of PMN-PT, but does not describe PLZT;[24] in this case the maxima of $\chi(\omega, T)$ are above T_C.

V. CONCLUSIONS

The purpose of the present study was to ascertain whether mobile defects, mainly O vacancies, interacting with polar nanoclusters or microdomains might be the origin of the memory in the susceptibility curves versus temperature of aging stages also above the relaxor transition; both dielectric susceptibility and elastic compliance have been tested.

In one experiment, we started from the well-behaved relaxor composition PLZT 9/65/35, presenting from 80% to full memory recovery of aging stages both in the dielectric and elastic curves, and introduced all conceivable types of extrinsic mobile defects: O vacancies, hydrogen defects and free charges from the ionized defects. As a result, the memory was almost unaffected or depressed, excluding that such defects are the main responsible for the high-temperature memory.

In another experiment we tested PLZTN 7/60/40, whose composition is very close to PLZT 9/65/35, but has mixed relaxor and ferroelectric properties and, due to the cation stoichiometry, should contain about 2 mol% O vacancies to ensure charge neutrality. This composition presents almost no memory imprinting, on the time scale of the previous experiments (1 day), again demonstrating that the interaction between mobile defects and polar clusters or ferroelectric microdomains cannot give rise to memory phenomena as found in relaxors and spin glasses. On the other hand, memory in the defective system is imprinted on a much longer time scale (months), suggesting that in this case the migration and reorientation of defects in the field of well developed ferroelectric domains occurred.

These findings show that the memory phenomena typical of certain canonical spin glasses and found in some relaxor ferroelectrics are intrinsic of the relaxor state also above the freezing temperature for the polar fluctuations. A comparison is made with $Y_{0.7}Ca_{0.3}MnO_3$, where the spin glass state is preceded by short-range ferromagnetic order,[7] and with superparamagnetic systems, where it is possible to tune both the width of the relaxation times of the relaxing units and their degree of interaction.

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